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(54) **ELECTROLYTIC SOLUTION AND BATTERY**

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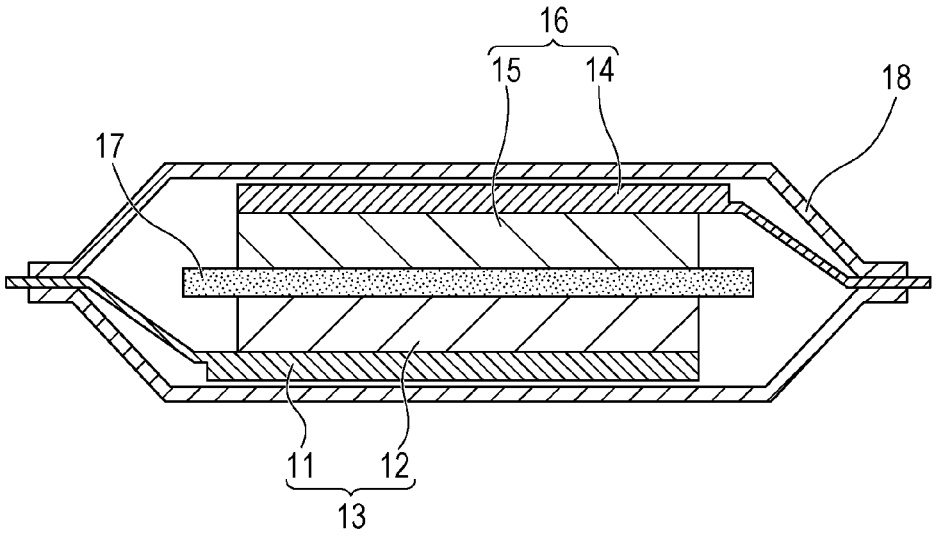
(57) **ABSTRACT**

Provided is an electrolytic solution including a nonaqueous solvent and an alkali metal salt. The alkali metal salt is dissolved in the nonaqueous solvent. The nonaqueous solvent contains a perfluoropolyether and a fluorinated phosphate. Also provided is a battery including the electrolytic solution, a positive electrode containing a positive electrode active material that can occlude and release an alkali metal cation, and a negative electrode containing a negative electrode active material that can occlude and release the alkali metal cation.

7 Claims, 1 Drawing Sheet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ELECTROLYTIC SOLUTION AND BATTERY

BACKGROUND

1. Technical Field

The present disclosure relates to an electrolytic solution for batteries and a battery including the electrolytic solution.

2. Description of the Related Art

Japanese Unexamined Patent Application Publication No. 2006-269374 discloses a lithium ion battery including an electrolytic solution containing a room temperature molten salt electrolyte comprising a perfluoropolyether.

In the electrolytic solution disclosed in Japanese Unexamined Patent Application Publication No. 2006-269374, the perfluoropolyether is added to the room temperature molten salt electrolyte in a proportion of 0.2% or more and 5% or less.

SUMMARY

One non-limiting and exemplary embodiment provides an electrolytic solution having higher safety, which has been demanded in known techniques.

In one general aspect, the techniques disclosed here feature an electrolytic solution containing a nonaqueous solvent and an alkali metal salt. The alkali metal salt is dissolved in the nonaqueous solvent. The nonaqueous solvent contains a perfluoropolyether and a fluorinated phosphate. In one general aspect, the techniques disclosed here feature a battery including the above-mentioned electrolytic solution, a positive electrode containing a positive electrode active material that has a property of occluding and releasing an alkali metal cation, and a negative electrode containing a negative electrode active material that has a property of occluding and releasing the alkali metal cation.

The present disclosure can achieve an electrolytic solution having high safety.

Additional benefits and advantages of the disclosed embodiments will become apparent from the specification and drawings. The benefits and/or advantages may be individually obtained by the various embodiments and features of the specification and drawings, which need not all be provided in order to obtain one or more of such benefits and/or advantages.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE is a schematic cross-sectional view illustrating an example of the battery according to Embodiment 2.

DETAILED DESCRIPTION

Embodiments of the present disclosure will now be described.

The viewpoints of the present inventor are described below.

Perfluoropolyethers and molecules having a perfluoropolyether skeleton have low compatibility to nonaqueous electrolytic solutions. Therefore, the amount of a perfluoropolyether or a molecule having a perfluoropolyether skeleton that can be added to a nonaqueous electrolytic solution is disadvantageously restricted to a narrow range.

For example, in Japanese Unexamined Patent Application Publication No. 2006-269374, the amount of the perfluoropolyether is limited to 5% or less.

Thus, if a perfluoropolyether is added to a nonaqueous electrolytic solution in an amount higher than a certain proportion (e.g., 5% or more), the perfluoropolyether cannot be uniformly mixed with the nonaqueous electrolytic solution, and the performance as an electrolytic solution cannot be shown.

On the basis of the above-mentioned viewpoints, the present inventor has arrived at the creation of the composition of the present disclosure.

Embodiment 1

The electrolytic solution in Embodiment 1 contains a nonaqueous solvent and an alkali metal salt.

The alkali metal salt is composed of an alkali metal cation and an anion.

The alkali metal salt is dissolved in the nonaqueous solvent.

The nonaqueous solvent contains a perfluoropolyether and a fluorinated phosphate.

In the composition described above, the alkali metal salt is sufficiently dissolved, and no phase separation occurs between the perfluoropolyether solvent and the fluorinated phosphate solvent as a third component. Accordingly, a perfluoropolyether can be mixed with a nonaqueous solvent at an arbitrary ratio and at a higher ratio. That is, a large amount of a perfluoropolyether can be uniformly mixed with a nonaqueous solvent. Consequently, for example, the electrolytic solution can have high flame retardancy, while keeping the function as an electrolytic solution. Thus, a nonaqueous electrolytic solution having higher safety can be achieved.

The perfluoropolyether is a flame retardant solvent and has a low polarity caused by the smallness in the fluctuation of electrons due to the large electronegativity of fluorine atoms. Consequently, the perfluoropolyether has low dissolving properties for salts and therefore cannot dissolve a large amount of a salt, unlike the solvents that are used in known nonaqueous electrolytic solutions.

The smallness of the polarity also causes low compatibility with usual organic solvents having high polarity. In other words, the low polarity prevents the perfluoropolyether from penetrating between the molecules of an organic solvent having a high polarity and large intermolecular forces. Consequently, the perfluoropolyether cannot be mixed with an organic solvent.

That is, in the viewpoint of the internal energy of a material, the internal energy form in the phase separated state is more stable than that in the uniformly compatibilized state.

As in stabilization of a polar organic solvent by the intermolecular forces derived from the polarity, the perfluoropolyether stabilizes the energy through the high affinity between fluorine atoms or intermolecular forces increasing with the molecular chain length.

The perfluoropolyether contained in the nonaqueous electrolytic solution of Embodiment 1 has a plurality of ether oxygen atoms in the molecule and has fluorine atoms substituted for the hydrogen atoms on all alkyl carbon atoms. For example, the perfluoropolyether of Embodiment 1 may be $CF_3—O—(CF_2—CF(CF_3)—O)_p—(CF_2—O)_q—CF_3$ or $CF_3—O—(C_3F_6—O)_p—(CF_2—O)_q—CF_3$.

The nonaqueous electrolytic solution of Embodiment 1 is used in, for example, a lithium secondary battery. Accordingly, the boiling point of the perfluoropolyether is preferably 60° C. or more, from the viewpoint of the general operation temperature of lithium secondary batteries. That

is, in order to achieve such a boiling point, the perfluoropolyether preferably has a weight-average molecular weight of about 350 or more.

An increase in the weight-average molecular weight causes an increase in the viscosity. Accordingly, the weight-average molecular weight is preferably also less than 1100.

The numbers, "p" and "q", of the repeating units in the chemical formula of the perfluoropolyether shown above are preferably selected such that the compound has a weight-average molecular weight of about 350 or more and 1100 or less. The perfluoropolyether may be a block copolymer or a random copolymer.

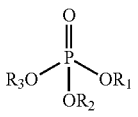
The perfluoropolyether may be a single compound or may be a compound having two or more different substituents or may be a mixture of structural isomers having the same substituent.

Herein, the weight-average molecular weight (Mw) is determined by multiplying the weight of each molecule by the molecular weight of the molecule, summing the resulting products, and dividing the resulting sum by the total weight.

Experimentally, the weight-average molecular weight can be determined by gel permeation chromatography (GPC) measurement. The GPC is one type of liquid chromatography for performing separation based on the difference in molecular size and is a method for measuring the molecular weight distribution and average molecular weight distribution of a high molecular weight material. In addition, use of a light scattering detector in the GPC can provide absolute molecular weight distribution and weight-average molecular weight of a polymer material and also information, such as the radius of rotation.

The perfluoropolyether can be synthesized by a known reaction, such as photooxidation of a perfluoroolefin or anionic polymerization of the epoxide of a perfluoroalkane. In the product synthesized by such a reaction, the degree of polymerization (i.e., the molecular weight of the product) varies depending on the degree of the reaction progress. A desired molecular weight of the product can be obtained by precision distillation or column purification.

In the electrolytic solution of Embodiment 1, the fluorinated phosphate may contain a compound represented by Formula (1):



(1)

where, R_1 to R_3 each independently represent an aromatic group, an unsaturated aliphatic group, or a saturated aliphatic group.

The aromatic group, the unsaturated aliphatic group, and the saturated aliphatic group may have at least one fluorine atom substituted for the hydrogen atom and may contain a halogen atom, a nitrogen atom, an oxygen atom, a sulfur atom, or a silicon atom.

The unsaturated aliphatic group and the saturated aliphatic group are straight chains or are cyclic.

The composition described above can sufficiently dissolve an alkali metal, has a high ionic conductivity, and also can provide an electrolytic solution having excellent resistance to oxidation. Consequently, the composition can contribute to the charging and discharging reaction of an active material that can provide a high voltage of a 4-V level.

As described above, in Embodiment 1, a fluorinated phosphate, which is an aprotic solvent, can be used.

The phosphate solvent has a P═O double bond composed of a phosphorus atom P and an oxygen atom O and having a large bond dipole moment. Accordingly, the phosphate solvent can strongly interacts with an alkali metal cation and can dissolve the alkali metal salt.

The substituents represented by R_1 to R_3 may be saturated aliphatic groups. In such a case, all the atoms bonding to carbon atoms may be hydrogen atoms or may be selected from hydrogen atoms and fluorine atoms.

In the electrolytic solution of Embodiment 1, the substituents R_1 to R_3 may be trifluoroethyl groups.

The trifluoroethyl group is represented by CF_3—CH_2—.

Such a structure is excellent in electrochemical stability, in the strength of interaction with an alkali metal cation, and in the compatibility with a perfluoropolyether solvent.

As described above, the fluorine-containing solvent can contribute to the charging and discharging reaction of an active material that can provide a high voltage.

The fluorine-containing polar solvent can have improved affinity with a perfluoropolyether molecule. Consequently, the influence on energy stabilization due to uniform compatibility can be enhanced.

In the electrolytic solution of Embodiment 1, the volume proportion of the perfluoropolyether to the nonaqueous solvent may be 10% or more and 75% or less.

For example, the alkali metal salt of Embodiment 1 may be represented by a formula "MX". The "M" of the alkali metal salt "MX" may be an alkali metal. The "X" of the alkali metal salt "MX" may be Cl, Br, I, BF_4, PF_6, CF_3SO_3, ClO_4, CF_3CO_2, AsF_6, SbF_6, $AlCl_4$, $N(CF_3SO_2)_2$, $N(FSO_2)_2$, $N(CF_3CF_2SO_2)_2$, or $N(CF_3SO_2)(FSO_2)$. The "X" of the alkali metal salt "MX" is preferably BF4, PF_6, ClO_4, $N(CF_3SO_2)_2$, or $N(CF_3CF_2SO_2)_2$ from the viewpoint of chemical stability, and is preferably $N(CF_3SO_2)_2$, $N(FSO_2)_2$, $N(CF_3CF_2SO_2)_2$, or $N(CF_3SO_2)(FSO_2)$ from the viewpoint of solubility. These alkali metal salts may be used alone or as a mixture of two or more thereof.

That is, the anion contained in the electrolytic solution of Embodiment 1 may be at least one selected from the group consisting of BF_4^-, PF_6^-, $N(SO_2CF_3)_2^-$, $N(SO_2F)_2^-$, $N(SO_2CF_2CF_3)_2^-$, $N(SO_2$—$CF_2CF_2SO_2$—$)^-$, and $[N$—(SO_2F)—$(SO_2CF_3)]^-$.

The composition described above can have improved solubility for an alkali metal salt and also can provide an electrolytic solution having a high ionic conductivity.

In the electrolytic solution of Embodiment 1, the alkali metal cation may be a lithium ion or a sodium ion.

Embodiment 2

Embodiment 2 will now be described, but the explanation duplicated with Embodiment 1 is appropriately omitted.

The battery in Embodiment 2 includes the electrolytic solution of Embodiment 1, a positive electrode, and a negative electrode.

The positive electrode contains a positive electrode active material that has a property of occluding and releasing (i.e., can occlude and release) one or more alkali metal cations.

The negative electrode contains a negative electrode active material that has a property of occluding and releasing (i.e., can occlude and release) the one or more alkali metal cations.

Such a configuration can provide a battery achieving a high voltage and having a high energy density.

The battery of Embodiment 2 can be constituted, for example, as a secondary battery.

FIGURE is a schematic cross-sectional view illustrating an example of the battery according to Embodiment 2.

The battery shown in FIGURE includes a positive electrode **13**, a negative electrode **16**, a separator **17**, and an outer package **18**.

The positive electrode **13** is composed of a positive electrode collector **11** and a positive electrode mixture layer **12** disposed on the positive electrode collector **11**.

The negative electrode **16** is composed of a negative electrode collector **14** and a negative electrode mixture layer **15** disposed on the negative electrode collector **14**.

The positive electrode **13** and the negative electrode **16** face each other with the separator **17** therebetween.

The positive electrode **13**, the negative electrode **16**, and the separator **17** are covered with the outer package **18** to form a battery.

The positive electrode mixture layer **12** may contain a positive electrode active material that can occlude and release alkali metal ions.

Examples of the positive electrode active material will now be described.

When the alkali metal is lithium, the positive electrode active material can be a known material that can occlude and release lithium ions. Examples of the positive electrode active material include transition metal oxides and lithium-containing transition metal oxides, for example, oxides of cobalt, oxides of nickel, oxides of manganese, oxides of vanadium such as vanadium pentoxide (V_2O_5), and mixtures or complex oxides thereof; complex oxides containing lithium and transition metals, such as lithium cobaltate ($LiCoO_2$); and silicates of transition metals and phosphates of transition metals such as lithium iron phosphate ($LiFePO_4$).

When the alkali metal is sodium, the positive electrode active material can be a known material that can occlude and release sodium ions. Examples of the positive electrode active material include transition metal oxides and sodium-containing transition metal oxides, for example, oxides of cobalt, oxides of nickel, oxides of manganese, oxides of vanadium such as vanadium pentoxide (V_2O_5), and mixtures or complex oxides thereof; complex oxides containing sodium and transition metals, such as sodium manganate ($NaMnO_2$); and silicates of transition metals and phosphates of transition metals.

The positive electrode collector **11** can be a porous or non-porous sheet or film made of a metal material, such as aluminum, stainless steel, titanium, or an alloy thereof. Aluminum and alloys thereof are inexpensive and can be readily formed into a thin film. The sheet or film can be, for example, metal foil or mesh. The surface of the positive electrode collector **11** may be coated with a carbon material, such as carbon, for reducing the resistance value, providing a catalytic effect, and enhancing the binding between the positive electrode mixture layer **12** and the positive electrode collector **11**.

The negative electrode mixture layer **15** may contain a negative electrode active material that can occlude and release alkali metal ions.

Examples of the negative electrode active material will now be described.

When the alkali metal is lithium, the negative electrode active material can be a known material that can occlude and release lithium ions. Examples of the negative electrode active material include lithium metal element, lithium metal alloys, carbon materials, and metal oxides. Examples of carbon material include graphite and non-graphite carbon materials, such as hard carbon and coke. Examples of the metal oxide include lithium titanate represented by $Li_4Ti_5O_{12}$. Examples of the lithium metal alloy include alloys of lithium with a silicon compound, tin compound, or aluminum compound.

When the alkali metal is sodium, the negative electrode active material can be a known material that can occlude and release sodium ions. Examples of the negative electrode active material include sodium metal element, sodium metal alloys, carbon materials, and metal oxides. Examples of carbon material include graphite and non-graphite carbon materials, such as hard carbon and coke. Examples of the metal oxide include sodium titanate represented by $Na_2Ti_3O_7$. Examples of the sodium metal alloy include alloys of sodium with a tin compound, germanium compound, zinc compound, bismuth compound, or indium compound.

The negative electrode collector **14** can be a porous or non-porous sheet or film made of a metal material, such as aluminum, stainless steel, nickel, copper, or an alloy thereof. Aluminum and alloys thereof are inexpensive and can be readily formed into a thin film. The sheet or film can be, for example, metal foil or mesh. The surface of the negative electrode collector **14** may be coated with a carbon material, such as carbon, for reducing the resistance value, providing a catalytic effect, and enhancing the binding between the negative electrode mixture layer **15** and the negative electrode collector **14**.

The positive electrode mixture layer **12** may contain a conductive assistant, an ion conductor, a binder, or another component.

The negative electrode mixture layer **15** may contain a conductive assistant, an ion conductor, a binder, or another component.

The conductive assistant can be used for reducing the electrode resistance. Examples of the conductive assistant include carbon materials, such as carbon black, graphite, and acetylene black; and conductive polymers, such as polyaniline, polypyrrole, and polythiophene.

The ion conductor can be used for reducing the electrode resistance. Examples of the ion conductor include gel electrolytes, such as polymethyl methacrylate; and solid electrolytes, such as polyethylene oxide.

The binder is used for improving the binding properties of the material constituting the electrode. Examples of the binder include polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymers, vinylidene fluoride-tetrafluoroethylene copolymers, polytetrafluoroethylene, carboxymethyl cellulose, polyacrylic acid, styrene-butadiene copolymer rubber, polypropylene, polyethylene, and polyimide.

The separator **17** can be a porous film made of, for example, polyethylene, polypropylene, glass, cellulose, or ceramic. The porous film can be used by filling the pores with an electrolyte.

EXAMPLES

Examples and Comparative Examples will describe nonaqueous electrolytic solutions as an aspect of the present disclosure, nonaqueous electrolyte secondary batteries produced using the nonaqueous electrolytic solutions, and the results thereof.

The nonaqueous electrolytic solutions in Examples were all prepared in an argon glove box.

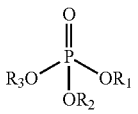
The composition of the present disclosure is not limited to the following Examples.

Example 1

Nonaqueous electrolytic solutions were prepared using the following perfluoropolyether, fluorinated phosphate solvent, and alkali metal salt.

That is, the perfluoropolyether used was a perfluoropolyether (manufactured by Solvay Specialty Polymers, Galden HT-80) having a weight-average molecular weight of 430.

The fluorinated phosphate solvent used was a compound (TFEP) represented by Formula (1):



(1)

where the substituents R_1 to R_3 are trifluoroethyl (CF_3—CH_2—) groups.

The alkali metal salt used was lithium bis(fluorosulfonyl) imide ($LiN(FSO_2)_2$).

The perfluoropolyether was mixed with the fluorinated phosphate (TFEP) at a volume proportion of the perfluoropolyether to the total volume (total volume of the solvents) of 10%.

Subsequently, the alkali metal salt was dissolved in the solvent mixture at a concentration of 0.36 M.

Nonaqueous electrolytic solution sample 1 was thus prepared.

Example 2

The same perfluoropolyether as that in Example 1 was mixed with the same fluorinated phosphate as that in Example 1 at a volume proportion of the perfluoropolyether to the total volume (total volume of the solvents) of 25%.

Nonaqueous electrolytic solution sample 2 was prepared as in Example 1 except the above.

Example 3

The same perfluoropolyether as that in Example 1 was mixed with the same fluorinated phosphate as that in Example 1 at a volume proportion of the perfluoropolyether to the total volume (total volume of the solvents) of 50%.

Nonaqueous electrolytic solution sample 3 was prepared as in Example 1 except the above.

Example 4

The same perfluoropolyether as that in Example 1 was mixed with the same fluorinated phosphate as that in Example 1 at a volume proportion of the perfluoropolyether to the total volume (total volume of the solvents) of 75%.

Nonaqueous electrolytic solution sample 4 was prepared as in Example 1 except the above.

Example 5

The solvent used was a perfluoropolyether (manufactured by Solvay Specialty Polymers, Galden HT-170) having a weight-average molecular weight of 760.

Nonaqueous electrolytic solution sample 5 was prepared as in Example 1 except the above.

Example 6

The solvent used was a perfluoropolyether (manufactured by Solvay Specialty Polymers, Galden HT-230) having a weight-average molecular weight of 1020.

Nonaqueous electrolytic solution sample 6 was prepared as in Example 1 except the above.

Comparative Example 1

Triethylene glycol dimethyl ether (CH_3—$(OCH_2CH_2)_3$—OCH_3) was used instead of the fluorinated phosphate in Example 1.

Nonaqueous electrolytic solution sample 7 was prepared as in Example 1 except the above.

Comparative Example 2

The same perfluoropolyether as that in Comparative Example 1 was mixed with the same triethylene glycol dimethyl ether as that in Comparative Example 1 at a volume proportion of the perfluoropolyether to the total volume (total volume of the solvents) of 25%.

Nonaqueous electrolytic solution sample 8 was prepared as in Comparative Example 1 except the above.

Comparative Example 3

Monoethylene glycol dimethyl ether (CH_3—$(OCH_2CH_2)_1$—OCH_3) was used instead of the fluorinated phosphate in Example 1.

Nonaqueous electrolytic solution sample 9 was prepared as in Example 1 except the above.

Comparative Example 4

The same perfluoropolyether as that in Comparative Example 3 was mixed with the same monoethylene glycol dimethyl ether as that in Comparative Example 3 at a volume proportion of the perfluoropolyether to the total volume (total volume of the solvents) of 25%.

Nonaqueous electrolytic solution sample 10 was prepared as in Comparative Example 3 except the above.

Comparative Example 5

Triethyl phosphate was used instead of the fluorinated phosphate in Example 1.

Nonaqueous electrolytic solution sample 11 was prepared as in Example 1 except the above.

Comparative Example 6

The same perfluoropolyether as that in Comparative Example 5 was mixed with the same triethyl phosphate as that in Comparative Example 5 at a volume proportion of the perfluoropolyether to the total volume (total volume of the solvents) of 25%.

Nonaqueous electrolytic solution sample 12 was prepared as in Comparative Example 5 except the above.

[Evaluation of Compatibility and Conductivity]

The nonaqueous electrolytic solutions of Examples 1 to 6 and Comparative Examples 1 to 6 were visually evaluated for compatibility. The nonaqueous solvents judged to be

uniform were measured for the conductivity. The conductivity was measured at 60° C.

Table 1 shows the results of evaluation of the compatibility and the conductivity of the nonaqueous electrolytic solutions of Examples 1 to 6 and Comparative Examples 1 to 6.

TABLE 1

	Weight-average molecular weight of perfluoropolyether	Second component other than perfluoropolyether	Volume proportion of perfluoropolyether [%]	Evaluation results of compatibility	Conductivity [10^{-6} S/cm]
Example 1	430	Fluorinated	10	○	814
Example 2		phosphate	25	○	510
Example 3			50	○	140
Example 4			75	○	8.84
Example 5	760		10	○	772
Example 6	1020		10	○	698
Comparative Example 1	430	Triethylene glycol dimethyl ether	10	X	—
Comparative Example 2			25	X	—
Comparative Example 3		Monoethylene glycol dimethyl ether	10	X	—
Comparative Example 4			25	X	—
Comparative Example 5		Triethyl phosphate	10	X	—
Comparative Example 6			25	X	—

In Table 1, "compatibility: x" means that deposition of the alkali metal salt or phase separation of the solvents was observed.

In Table 1, "compatibility: ○" means that no deposition of the alkali metal salt or no phase separation of the solvents was observed.

As shown in Table 1, the nonaqueous electrolytic solutions of Examples 1 to 6 were prepared as uniform electrolytic solvents that did not cause phase separation even in the case of containing a volume proportion of 10% or more of the perfluoropolyether.

In particular, the nonaqueous electrolytic solutions of Examples 1 to 4 each containing a perfluoropolyether having a molecular weight of 430 and a fluorinated phosphate were uniformly mixed in a broad composition range, i.e., in a volume proportion of the perfluoropolyether solvent of 10% to 75%.

In contrast, nonaqueous electrolytic solution samples 7 to 12 of Comparative Examples 1 to 6 containing nonaqueous solvents that are usually used as the nonaqueous electrolytes for lithium secondary batteries instead of the fluorinated phosphate were not uniform, and phase separation was observed.

It was accordingly demonstrated that the fluorinated phosphate works for dissolving an alkali metal salt and for preparing a uniform solution.

The phosphate ester group of triethyl phosphate used in Comparative Examples 5 and 6 is ethyl group and differs from the trifluoroethyl group used in Examples 1 to 6 in whether fluorine is contained or not. The electrolytic solutions of Examples 1 to 6 were uniformly compatible, whereas the electrolytic solutions of Comparative Examples 5 and 6 caused phase separation. This demonstrated that an unsubstituted phosphate is insufficient for preparing a uniform solution, and a fluorinated phosphate is effective.

Example 7

Example 7 relates to a lithium secondary battery containing a nonaqueous electrolytic solution.

The positive electrode active material was $LiNiCoAlO_2$.

The positive electrode active material, acetylene black as a conductive assistant, and polyvinylidene fluoride as a binder were weighed at a weight ratio of 8:1:1, and the mixture was dispersed in an NMP solvent to prepare a slurry.

The resulting slurry was applied to an Al collector with a coater.

The electrode plate coated with the slurry was rolled with a rolling mill, was punched into a 20 mm square, and was processed into an electrode state to prepare a positive electrode.

A negative electrode was produced by pressure-bonding lithium metal to a 20 mm square nickel mesh.

The positive electrode and the negative electrode were disposed so as to face each other with a polyethylene microporous film as the separator therebetween to produce an electrode group having a configuration described in Embodiment 2.

Nonaqueous electrolytic solution sample 3 of Example 3 was used as the electrolytic solution.

The electrolytic solution was poured to the electrode group, and sealing was performed to produce a laminated lithium secondary battery.

[Charging and Discharging Test]

The lithium secondary battery of Example 7 was subjected to a charging and discharging test under the following conditions.

The charging and discharging test was performed in a thermostatic chamber of 60° C.

In the test, charging was first performed, and the battery was paused for 30 minutes, followed by discharging. This charging and discharging were repeated three times.

The charging was performed at a constant current and a constant voltage with a current of 0.05 C rate with respect to the theoretical capacity of the positive electrode active material. The upper limit charging voltage was 4.2 V. The lower limit current value at the constant voltage was 0.02 C rate.

The discharging was performed at a lower limit discharging voltage of 2.5 V and a current of 0.05 C rate. After pausing for 30 minutes, discharging was performed at a current of 0.02 C rate.

The charging and discharging operation was repeated three times. On this occasion, stable charging and discharging operation was confirmed. After the confirmation, the discharging capacity on the third discharging operation was converted into the capacity per 1 g of each positive electrode active material ($mAhg^{-1}$).

Table 2 shows the resulting discharging capacities.

TABLE 2

	Solvent composition		
	Solvent other than perfluoropolyether	Volume proportion of perfluoropolyether [%]	Discharge capacity [$mAhg^{-1}$]
Example 7	Fluorinated phosphate (TFEP)	50	210

The electrolytic solutions of Comparative Examples 1 to 6 caused phase separation and could not be subjected to the charging and discharging test.

In contrast, as shown in Table 2, the battery of Example 7 had a discharging capacity of 210 $mAhg^{-1}$.

The results demonstrated that the electrolytic solution of Example 7 had sufficient electrochemical stability capable of withstanding charging and discharging operation of the battery, in spite of a large amount (a volume proportion of 50%) of the perfluoropolyether, which is a flame retardant, contained in the electrolytic solutions.

The electrolytic solution of the present disclosure can be used as the electrolytic solution of a battery.

What is claimed is:

1. An electrolytic solution comprising:

a nonaqueous solvent; and

an alkali metal salt, wherein

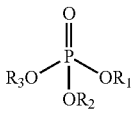
the alkali metal salt is dissolved in the nonaqueous solvent; and

the nonaqueous solvent contains a perfluoropolyether and a fluorinated phosphate,

wherein the perfluoropolyether is $CF_3—O—(CF_2—CF(CF_3)—O)_p—(CF_2—O)_q—CF_3$ or $CF_3—O—(C_3F_6—O)_p—(CF_2—O)_q—CF_3$, wherein p and q are selected so that the perfluoropolyether has a weight average molecular weight of about 350 to less than 1100.

2. The electrolytic solution according to claim **1**, wherein

the fluorinated phosphate contains a compound represented by Formula (1):



(1)

where, R_1 to R_3 each independently represent an aromatic group, an unsaturated aliphatic group, or a saturated aliphatic group, wherein

the aromatic group, the unsaturated aliphatic group, and the saturated aliphatic group has at least one fluorine atom substituted for the hydrogen atom and contains a halogen atom, a nitrogen atom, an oxygen atom, a sulfur atom, or a silicon atom; and

the unsaturated aliphatic group and the saturated aliphatic group are straight chains or are cyclic.

3. The electrolytic solution according to claim **2**, wherein

R_1 to R_3 represent trifluoroethyl groups.

4. The electrolytic solution according to claim **1**, wherein

the nonaqueous solvent contains the perfluoropolyether at a volume proportion of the perfluoropolyether to the nonaqueous solvent of 10% or more and 75% or less.

5. The electrolytic solution according to claim **1**, wherein

the alkali metal salt is composed of an alkali metal cation and an anion; and

the anion is at least one selected from the group consisting of BF_4^-, PF_6^-, $N(SO_2CF_3)_2^-$, $N(SO_2F)_2^-$, $N(SO_2CF_2CF_3)_2^-$, $N(SO_2—CF_2CF_2SO_2—)^-$, and $[N—(SO_2F)—(SO_2CF_3)]^-$.

6. The electrolytic solution according to claim **1**, wherein

the alkali metal salt is composed of an alkali metal cation and an anion; and

the alkali metal cation is a lithium ion or a sodium ion.

7. A battery comprising:

an electrolytic solution;

a positive electrode containing a positive electrode active material that has a property of occluding and releasing an alkali metal cation; and

a negative electrode containing a negative electrode active material that has a property of occluding and releasing the alkali metal cation, wherein

the electrolytic solution contains a nonaqueous solvent and an alkali metal salt;

the alkali metal salt is composed of the alkali metal cation and an anion;

the alkali metal salt is dissolved in the nonaqueous solvent; and

the nonaqueous solvent contains a perfluoropolyether and a fluorinated phosphate, wherein the perfluoropolyether is $CF_3—O—(CF_2—CF(CF_3)—O)_p—(CF_2—O)_q—CF_3$ or $CF_3—O—(C_3F_6—O)_p—(CF_2—O)_q—CF_3$, wherein p and q are selected so that the perfluoropolyether has a weight average molecular weight of about 350 to less than 1100.

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